A New Energetic Mixed Formal Plasticizer, Using Diformal as Eutectic Material

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ABSTRACT

BDNPF/A is a useful energetic plasticizer, but mixed formal, which consists of BDNPF, DNPBF, and BDNBF, is anticipated to be better than BDNPF/A in chemically, thermally and economically. Last year, we successfully synthesized and characterized the mixed formal that has minimum contents of diformal. It is well known that the existing mixed formal always has an 8 ~ 10 % of diformal. At first, we attempted to reduce the diformal content. During this study, we have got the ability to control diformal content variably. In order to control the diformal content, synthetic procedure and reaction condition were modified and adjusted precisely. From this result, we used the diformal as a new eutectic agent and proposed the new component of mixed formal. The thermogravimetry (TG) analysis of the new mixed formal plasticizer shows an acceptable stability for practical applications. This new plasticizer is expected to be cheaper than the existing mixed formal because only one compound of starting material, DNP-OH, is required, DNB-OH will not be used for this process, and the yield of formalization reaction was increased from 75% to more than 90%. Furthermore, this plasticizer does not crystallize at -20 . Finally, we confirmed that the diformal is more effective than the existing eutectic material produced with DNB-OH.

The synthesis, characteristics and application of the new two-component mixed formal will be discussed.

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BACKGROUND

DOA (dioctyl adipate), IDP (isodecyl pelargonate), BTTN (butanetriol trinitrate), TMETN (trimethylol ethane trinitrate), and DEGDN (diethylene glycol dinitrate) have been widely used as the plasticizers in PBXs (plastic-bonded-explosives), gun propellants, and rocket propellants. But these plasticizers have several shortcomings. DOA and IDP are inert materials, which are non-energetic in nature. BTTN, TMETN and DEGDN are energetic materials, but somewhat migrating, volatile and unstable in high temperature aging because of nitrate ester. Therefore, Some energetic plasticizers containing nitro group, which show the thermal stability, had been developed, used and new energetic plasticizers are still being searched [1].

One of the commercially available nitroplasticizers is BDNPF/A. It has been manufactured according to the ter Meer process for over three decades [2]. Recently, an

environmentally favorable synthetic method [3] and continuous process [4] of BDNPF/A have been developed and utilized into a full-scale manufacturing process. BDNPF/A is a useful energetic plasticizer, but a significant shortcoming of this material is the limited chemical and thermal stability of BDNPA. The acetal group in BDNPA is known to be thermally and chemically less stable than the formal group in BDNPF [5]. Furthermore, BDNPF/A is expected to be more or less expensive because BF_3OEt_2 (boron trifluoride diethyletherate) and acetaldehyde should be used during the formalization.

Another energetic plasticizer, a eutectic mixture of BDNPF, DNPBF and BDNBF, was well known as a new low cost energetic nitroplasticizer, which has good chemical and thermal stability [5]. We successfully synthesized the F/F plasticizer, but these F/F plasticizers have some disadvantage. First, F/F plasticizer could be recrystallized under long-term storage test at –20 ^{o}C. Second, The produced F/F plasticizers always contain 8~10% of diformal that may slightly decrease the energy of energetic plasticizer. Last year, we successfully synthesized and characterized the mixed formal that has minimum contents of diformal. At first, we attempted to reduce the diformal content. During this study, we have got the ability to control diformal content variably. In order to control the diformal content, synthetic procedure and reaction condition were modified and adjusted precisely. From this result, we used the diformal as a new eutectic agent and proposed the new component of mixed formal. The thermogravimetry (TG) analysis of the new mixed formal plasticizer shows an acceptable stability for practical applications. This new plasticizer is expected to be cheaper than the existing mixed formal because only one compound of starting material, DNP-OH, is required, DNB-OH will not be used for this process, and the yield of formalization reaction was increased from 75% to more than 90%. Furthermore, this plasticizer does not crystallize at -20 . Finally, we confirmed that the diformal is more effective than the existing eutectic material produced with DNB-OH.

EXPERIMENTALS

2,2-Dinitropropanol (DNP-OH)

To study formalization reaction, we synthesized the DNP-OH, and potassium ferricyanide route developed by Baum [6] was tried first. After a lot of experiments, it was concluded that the yield of DNP-OH was low (59-63%) and the purity was not good enough to run formalization reaction directly without further purification. So the synthetic route described by Kaplan and Shechter [7] using $AgNO_3$ was tested and adjusted. Through the experiments, the conditions of oxidative nitration with silver nitrate and methylolation with 35% formalin solution were optimized. Under this optimized condition, the average yield of DNP-OH is over 90% and its purity is over 97%. As the extracting solvent, methylene chloride was used. When the solvent was evaporated, pale yellowish solid DNP-OH was obtained.

F/DF Mixed Formal

After suspension of the DNP-OH and predetermined amount of excess paraformaldehyde in CH_2Cl_2 at 5 , the concentrated H_2SO_4 was added to the reaction solution as possible as fast within 5 minute. After extracted with CH_2Cl_2, the organics were

washed with aqueous NaOH to remove residual acid and any unreacted alcohols. The solution was dried and concentrated to give the desired F/DF mixed-formal.

RESULTS & DISCUSSION

We propose a new two component energetic plasticizer (F/DF) consisted of BDNPF and BDNPDF.
F/DF plasticizers were synthesized and characterized. In order to control the diformal content, synthetic procedure and reaction condition were modified and adjusted precisely. From this result, we used the diformal as a new eutectic agent and proposed the new component of mixed formal.

Synthesis of BDNPF/BDNPDF Mixed Formal

Generally it is known that the formal can be generated from the mixture of alcohol and formaldehyde through the dehydrating with concentrated sulfuric acid. 3-Component mixed-formal (BDNPF/DNPBF/BDNBF) also can be synthesized with this current method.

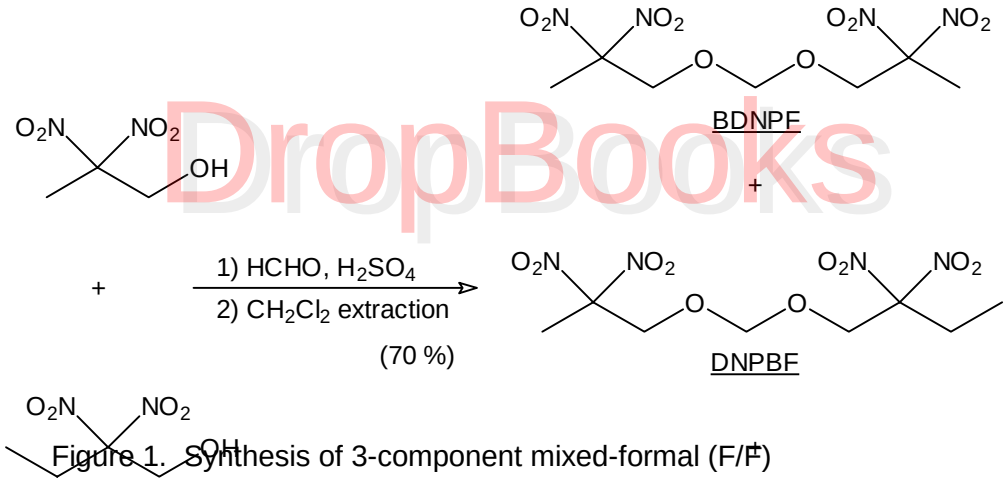
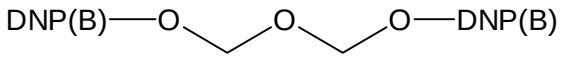


Figure 1. Synthesis of 3-component mixed-formal (F/F)

When the suspension of the mixed alcohol (DNP-OH: DNB-OH = 3: 1) and paraformaldehyde in CH_2Cl_2 was treated with concentrated H_2SO_4, the wanted mixed formal could be made. But, in the synthesized mixed-formal, there was one major side product. About 10% of diformal existed in it beside of 3 kinds of formal.



At first, we attempted to get rid of this diformal, if it is impossible; to minimize the impurity content, modification of synthetic procedure was attempted. Last year, we reported the F/F plasticizer with minimum contents of diformal about 3~4%. Finally, we have some ability to control diformal content from 8% to 40%. If we add paraformaldehyde as rapid feeding more than required equivalent, the diformal was produced and controlled with

paraformaldehyde.
On the course of this study, we adopted this diformal as a eutectic material.

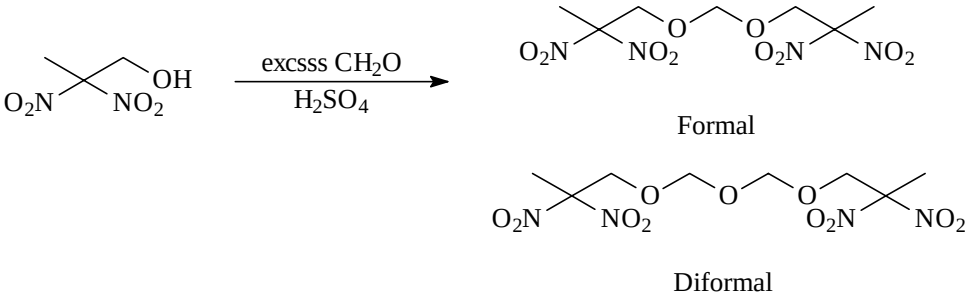


Figure 2. Synthesis of 2-component mixed-formal (F/DF)

The produced F/DF mixed formal was analyzed by ^{1}H-NMR and calculated the diformal content based on the proton $-CH_3$ at 2.2ppm.

Table 1. The results of diformal control reaction with different content of formaldehyde

Mole ratio P/T/SAc[a]	Diformal, % (NMR results)[b]	Yield[c], % ( )[d]	Remark[e]
2/1.0/3	9.1	87.0 (86.3)	Sulfuric acid feeding for 5 min.
2/1.1/3	8.0	88.0 (87.4)	Trioxane solution in sulfuric acid added for 3 min
2/1.3/3	24	90.9 (88.6)	Sulfuric acid feeding for 5 min
2/1.5/3	25.9	91.0 (88.5)	Sulfuric acid feeding for 5 min
2/2.0/3	38.0	93.0 (89.2)	Sulfuric acid feeding for 5 min
2/3.3/3	40.1	80.5	Sulfuric acid slowing feeding

a : P/T/SAc is the mole ratio of DNP-OH/s-Trioxane/H_2SO_4
b : Calculated results of Diformal content based on 2.2ppm
c : Apparent yield,
d: True yield, calibrated by molecular weight of diformal

Figure 3. Typical ^{1}H-NMR spectra of F/DF mixed formal

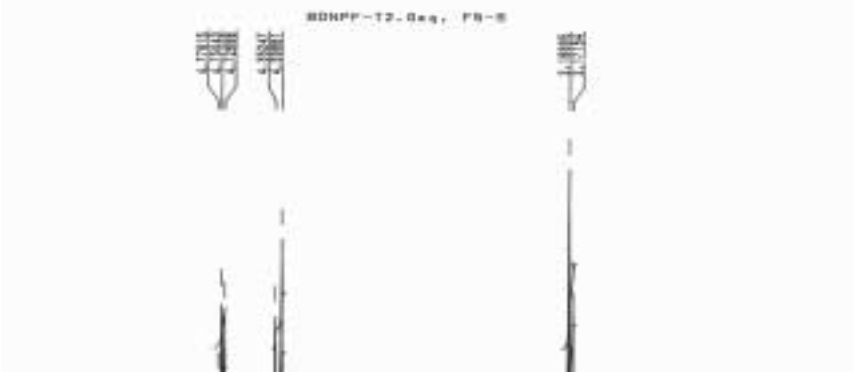
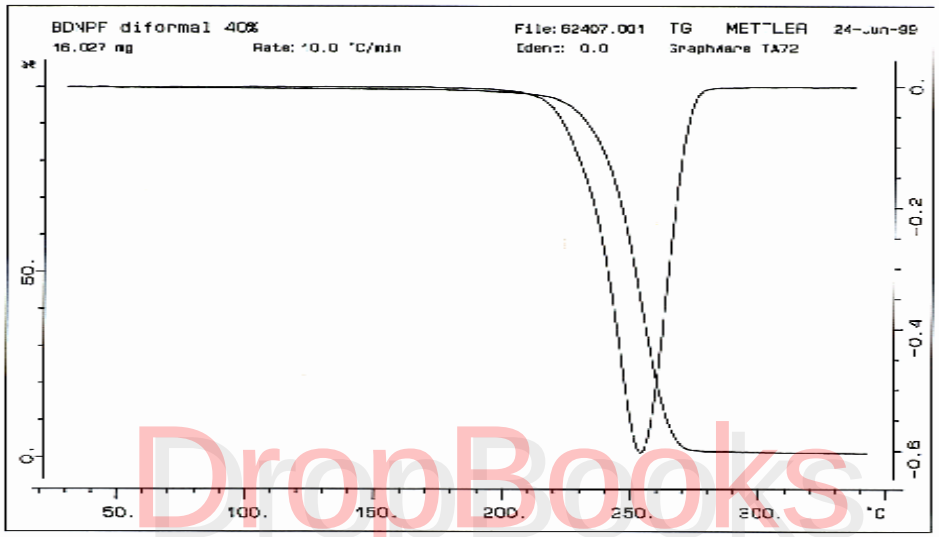


Figure 4. TG thermogram of F/DF mixed formal



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From Figure 3, we confirmed the diformal peak at 2.2ppm and calculated the diformal content using this peak. Figure 4 shows that the thermal stability of F/DF plasticizer was similar to the existing F/F plasticizer. The F/DF plasticizer didn't crystallized for 3 months storage test at -20 , but F/F mixed plasticizer was crystallized. Therefore, we concluded that the thermal stability of F/DF was superior to F/F and it has a potential possibility for application.

CONCLUSION

A new energetic plasticizer consisting two-component mixed formal, which contains of BDNPF and BDNPDF, was synthesized and characterized. In order to control the content of eutectic material (BDNPDF), synthesis procedure was modified and adjusted precisely.

From this study, we can control the diformal contents variably and synthesized F/DF mixed-formal shows an acceptable stability for practical applications. This F/DF plasticizer shows excellent physical stability at long-term storage test.

Finally, this new plasticizer is expected to be cheaper than the existing mixed formal because only one compound of starting material, DNP-OH, is required. DNB-OH will not be used for this process, and the yield of formalization reaction was increased from 75% to more than 90%.

PLANS FOR FUTURE WORK

The scale-up process for manufacturing of F/DF will be performed at the end of this year and formulation research in the developing insensitive explosives and propellants is still on going by our formulators.

ACKNOWLEDGEMENT

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